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16. ABSTRACT A data base of existing metal corrosion data has been compiled by the National Bureau of Standards. The data base contains only exposure studies that were conducted according to standard ASTM procedures and had adequate documentation of the site characteristics and period of exposure. This report presents work conducted at Washington University to examine the exposure data for evidence of key features which may clarify the likely importance of man-made pollutants on the corrosion of metals.		
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1. INTRODUCTION

The corrosion of metals exposed to the atmosphere is known to be caused by a mixture of natural and anthropogenic factors. To apportion the cause of metal corrosion, one may conduct controlled laboratory experiments or well designed field exposure experiments. A complicating factor may arise in the case that the progress of corrosion is not constant in time, but may change significantly after an initial period, e.g. due to erosion or formation of protective surface layers. Such erratic behavior has been documented by Guttman (1968) for variability of zinc corrosion with season of first exposure. Therefore it is also desirable to examine the records of long term exposure studies to better reflect the actual fate of exposed metals. Unfortunately, the environmental data associated with such exposures are generally insufficient to document the meteorological and chemical causes of the corrosion.

The usefulness of existing long term exposure metals corrosion data thus depends upon reconstruction of the meteorological and chemical histories which are relevant to corrosion. To do so involves analysis of data on meteorology and pollutant emissions in conjunction with data interpolation tools, i.e. pollutant dispersion models. This report discusses the current status of such an effort at Washington University, and examines the existing exposure data for evidence of key features which may clarify the likely importance of manmade pollutants in metals corrosion.

2. METAL CORROSION DATA

The existing long term exposure metal corrosion data has been reported in a number of papers in journals and proceedings over the years. The considerable task of locating, verifying, standardizing and assembling the numerous bits of information into a coherent whole was undertaken by E. Escalante of the National Bureau of Standards. Thus, the final data set contains only those experiments which were conducted according to standard ASTM procedures and had adequate documentation of the site characteristics and period of exposure.

The corrosion data includes periods from 1936 to 1978, with exposure durations of 1 to 20 years. Most data refer to the period of the 1960s, and reflect durations of 1 to 7 years. The sites are predominantly in the eastern United States or in California.

Six metals are included in the assembled records: carbon steel, weathering steel, galvanized steel, zinc, aluminum, and bronze. A total of 63 sites are found in the data base, with many sites reporting values for numerous metals. Sites were classified as marine, industrial, or urban. The site distribution is given below.

METAL	Sites	Rural	Marine
Aluminum	17	5	6
Bronze	9	5	4
Galvanized Steel	15	9	2
Weathering Steel	4	2	1
Zinc	35	8	10
Carbon Steel	48	10	16

The parameters for the corrosion data include site location and classification, duration and time period of exposure, source reference, and a series of corrosion measures: corrosion rate ($\text{mg}/\text{dm}^2/\text{da}$, or mdd), percentage change in strength and elongation, pit depth, years to first rust, and others which were rarely used. The change in strength and in elongation are more directly important as measures of structural integrity than is the more commonly measured weight loss measure of mdd.

In the process of examining the metal corrosion data, care was taken to average only over narrow time ranges. A graphical presentation of the averaged data values is contained in the final report associated with the metal corrosion study (Patterson and Husar, 1985). The reader is referred to that report for the details of the data set. In this paper we present some key results.

3. PARADIGM

The retrospective study has been formulated with a clear paradigm of the parameters of the corrosion system. It is assumed that the significant contributors to the corrosion of metals exposed to the atmosphere are water, sea salts, sulfur oxides, nitrogen oxides, and the acidity of precipitated water.

In the absence of water, it is presumed that no significant corrosion activity will take place. Surfaces may be moist due to precipitation, dew, hygroscopic action, and other causes. Precipitation is presumed to act in three modes: by cleansing the surface of accumulated dry deposited matter, by moistening the surface, and (at low pH) by direct chemical attack upon the metal and corrosion products.

In the presence of moisture, it is assumed that the key chemical reactions are initiated by SO_2 and perhaps by NO_x gases. Other mechanisms, such as dry deposition of acidic aerosol or deposition of HNO_3 to dry surfaces, are not considered. Synergistic effects are similarly disregarded.

With this outlook, the key factors appear to be the coincident occurrence of SO_2 and moisture. The controlled metal exposures from the ASTM studies were of flat panels in standard orientation. The simple geometry avoids many complications from moisture retained in surface texture features. Therefore, as a first approximation, we take the relevant time of wetness to be short periods following precipitation and periods of dew formation. The formation of a film of water is most likely at high relative humidities; high humidities are most prevalent during the night hours. In the eastern U.S., summer predawn humidity is typically 80-90% compared to afternoon humidities of 50-60%; winter patterns are less pronounced in areas north of the Ohio river, but also show afternoon minima (Baldwin, 1973).

The impact of near surface and elevated emission sources of SO_2 on surface concentrations has been shown to differ very strongly (Husar et al., 1978). Elevated emission sources contribute little to night time SO_2 concentrations, with the plume typically touching down in midmorning during summer conditions. Near surface emissions, however, cause high concentrations of SO_2 (and NO_x) overnight. These surface source emissions are trapped within a shallow nocturnal mixing layer with relatively little dispersion, thus making SO_2 available at the same time that moisture is most likely to be present. The "corrosion potential" for nearby surface sources is thus disproportionately large for its emissions.

4. RETROSPECTIVE RECONSTRUCTION OF ENVIRONMENTAL HISTORIES

The reconstruction of the pollutant concentrations to which a material is likely to have been exposed requires both emission information and diffusion models to relate emission trends to ambient concentrations downwind.

Using historical archives of fuel use, Husar (National Academy of Sciences, 1984) has developed and applied a methodology for estimating the historical SO_2 emissions on a state by state basis back to 1900. No such central record exists, unfortunately, for emissions on the urban scale.

The CAPITA Monte Carlo regional model of pollutant transmission through the atmosphere was developed as a diagnostic tool to simulate the formation and transport of sulfate aerosol. It has subsequently been modified and applied to simulation of sulfur wet deposition as well as sulfate concentration (Husar et al., 1985 a,b). For the current purposes, the model was substantially modified in order to adequately model the diurnal patterns of SO_2 impact from near surface and elevated sources. The simulation is appropriate for the regional scale, with time step of 3 hours and spatial resolution of about 100 km in a grid of roughly 12000 km^2 . This scale, however, is inadequate for simulation of primary pollutants such as SO_2 within the first 100- 200 km of transport. The average over the grid, even if correct, does not reveal the orders of magnitude higher concentrations experienced in small areas nearest the sources of emissions.

Therefore a local model was developed to better simulate the near field concentration and deposition impacts of primary emissions. This simulation utilizes much of the same formulation in terms of meteorology as the regional model (with improved initial vertical dispersion simulation), and with identical kinetics for transformation of SO_2 to $\text{SO}_4^{=}$, dry deposition of sulfur, and wet deposition of sulfur. This model was used to estimate correction factors to be applied to the regional model results.

The full methodology of retrospective analysis was applied for the case of marble tombstone deterioration in an urban and a remote cemetery near New York City (Husar et al., 1985 c,d). In this exercise it was found that our technique may estimate rural SO_2 concentrations acceptably well, but it does not reproduce detailed structure of urban concentrations adequately. The main reasons are uncertainty about the effective release heights of sources and a lack of detailed local emission information. For the purposes of metal corrosion, the current state of the retrospective reconstruction of environmental histories is not sufficiently quantitative to warrant extraction of damage functions.

The data set of metal corrosion provides a valuable insight as to which parameters dominate the corrosion process. The general meteorological features are well established in North America (although micrometeorological factors may dominate at any single exposure site). The pollutant related questions may be simply stated: (1) what are the magnitudes of marine and industrial corrosion rates compared to the rural values; (2) what are the relative rates in the rural eastern United States compared to the western rural values; (3) what are the broad trends in corrosion rate over the years?

Roughly speaking, the first question addresses the importance of SO_2 , while the second and third relate to the regional scale impacts of SO_2 , $\text{SO}_4^{=}$, and acidic deposition. SO_2 in urban areas is a matter for local control efforts, whereas the regional impacts (which are due to long range transport of emitted material) require larger scale controls and fall into the category of "acid rain" associated damage.

5. OBSERVATIONS

This section discusses a few of the major patterns evident in the metals corrosion database. In many respects, the results are restatements of the findings of earlier research by those associated with the original projects. For the purposes of the retrospective reconstruction project, it is nevertheless useful to determine whether the initial assumptions appear reasonable and to examine the relative importance of the meteorological and chemical factors as revealed in the data. This will tell where to place additional effort for the best improvement. More specifically, if the aim of the study is to explain the observed variations in corrosion rate, we first wish to know what variations are strong enough to warrant further study.

First the data were examined for variability. The convenient measure of noise to signal (standard deviation divided by the mean) yielded values which were quite large for a large number of carbon steel exposure tests. Due to this variability and the typically short exposure times, carbon steel was not examined in greater detail. Single year exposures of zinc plates indicated that the relative variability was 30% for marine sites, 20% for rural sites, and 10% for industrial sites. The marine sites had the highest corrosion rates as well as the highest relative variability, while the industrial sites indicated rather consistent behavior even over this short time period. At the other extreme, bronze triplicate panels yielded relative variability of below 10% after 20 year exposures. The overall result of such considerations was the decision to average data wherever multiple values were available with nearly identical exposure times. Similarly, it indicated that small differences in corrosion rates (particularly during the first few years) should not be overinterpreted.

The near coastal effect of wetness and sea salt is evident in the data, particularly for 1 and 2 year exposures. Zinc corrosion rates at Cape Kennedy, FL, dropped by a factor of 4 as distance from the coast increased from 60 to 880 m. At Kure Beach, NC, Zn rates dropped by a factor of 3 as distance increased from 25m to 250m from sea; corresponding Al corrosion rates fell by a factor of 2. Clearly sites within a few hundred meters of the sea must be segregated from other sites in any further analysis.

The general meteorological environment in the continental U.S. is well known, ranging from the desert Southwest to the roughly 1m annual rainfall over much of the country east of the Mississippi river. The number of days with measurable precipitation is about 50% higher in the northeastern quadrant of the nation than in the Great Plains. The number of days with heavy fog is higher by a factor of 2 or more in the mountainous portions of the eastern U.S. and in coastal areas than in the Great Plains or lower Ohio River valley (Baldwin, 1973). Therefore some variation in corrosion rates within the eastern U.S. may be expected just from variation in time of wetness.

Four sites with multiple alloys exposed over the years recur in most of the metal corrosion data sets. These sites include rural marine exposures at Point Reyes, CA and Kure Beach, NC; industrial exposures at Newark, NJ; and an eastern U.S. rural inland location at State College, PA.

Aluminum alloys indicate generally low corrosion rates, except in the Chicago area; for several alloys, corrosion rates there were nearly an order of magnitude higher than at other sites. For AL 6061 (T6), the industrial environment caused substantial corrosion and loss of strength. For three other alloys (AL 2014 (T4), AL 2024 (T81) and AL 7075 (T6)), the higher rates were noted at the marine sites, with less industrial effect. For all these alloys, the rural Pennsylvania corrosion rates were lower than the corresponding rates at industrial sites, by a factor of 2 to 7 after 7 years exposure. The rural site exposures induced no significant strength loss. Therefore it may be tentatively concluded that the regional scale causes of aluminum corrosion are not sufficiently pronounced to warrant further research at this time.

Weathering steel data indicated rather constant corrosion rates after 8 year exposures (1967- 1975) at marine, urban and rural sites in the eastern U.S. Although this data is limited, it suggests that the corrosion history of this weathering steel alloy must be relatively insensitive to both SO_2 concentration and to the pH of rainfall. An alternative explanation is that pollutant levels above some threshold value are sufficient to induce the observed corrosion. Even so, the data do not offer clues as to the pollutant effect.

Galvanized steel data is available from 20 year exposures (1936-1956) and from 2 year exposures (1971-1973). The twenty year exposures show that corrosion rates in the Great Plains range from 0.2 to 0.4 mdd, while rural rates in the Ohio River valley and the northeastern U.S. range 0.5 to 0.6 mdd. Such rural differences are likely attributable to variations in time of wetness. Industrial exposures are associated with rates of 1-3 mdd.

The more recent short term exposures at the rural State College site indicate lower corrosion rates than were registered during the earlier 20 year exposures. Although it is difficult to make such comparisons, the suggestion that rural eastern U.S. corrosion rates have increased over the past several decades is not supported by these measurements.

Zinc provides the most extensive set of measurements among the metals. Data are available from 7 year exposures ending in 1956 and in 1965, as well as dual sets of 20 year exposures ending in 1951 and 1978. The data show strong dependence on presumed time of wetness. The two distinct 20 year exposure periods include use of the same site at State College, PA. At this rural site, the long term corrosion rates over the 1931- 1951 period were identical to those of the 1958- 1978 period. Thus the idea of increasing rural corrosion rates over the past 5 decades is not supported. Industrial corrosion rates are substantially higher than rural rates; during the earlier exposure study, neighboring sites indicated industrial rates 3 to 6 times higher than those recorded at rural sites.

These data do not offer enough spatial coverage to assess the differences between eastern and noneastern rural corrosion rates. The Interstate Surveillance Project (Cavendar et al., 1971) provided measures of zinc corrosion rates at a number of sites in the Great Plains south to Texas as well as in the eastern U.S. This data represents the effects after single year exposures, so that large variability is expected. A clear overall pattern is evident, however, which suggests that eastern U.S. rural corrosion rates for zinc are higher than the corresponding rates in the Great Plains by a factor of 2 to 3. This is more than can be accounted for by meteorological factors alone; it is presumed, therefore, that rural zinc corrosion rates in the eastern U.S. are affected to a significant degree by regional pollution. The regional effect is not likely to be a new phenomena.

Bronze data is sparse. An alloy of 92% Cu exposed from 1931- 1951 showed no corrosion in the desert environment and very little at the rural sites. Coincident zinc data indicates that over the 20 year period the average corrosion rates were higher for bronze at marine sites but much lower for bronze than for zinc at rural sites.

At the rural State College, PA, site the corrosion rate for two different bronze alloys during the 1958- 1978 period was nearly twice that of the earlier bronze exposure, while the industrial Newark area corrosion rates appeared to have declined.

A bronze with 99% Cu in alloy with 1.25% Sn and P was exposed during the 1958-1978 period at the four standard ASTM sites. The corrosion rates at the rural site and the western marine site were less than half those at the eastern marine and industrial sites. Chemical analyses of the corrosion product (Costas, 1982) indicated that no sulfur compounds were present at either of the marine sites; apparently pollutants did not cause the marine bronze deterioration. Over 90% of the corrosion product was still adhering at these marine sites after 20 years. At the rural site, 67% remained, while only 27% of the corrosion product remained at the industrial site.

A bronze alloy more representative of statuary bronzes (5% Sn and P) was also exposed at the four standard sites. The rural and western marine sites again show corrosion rates less than half those of the eastern marine and the industrial site. The corrosion rates at the industrial and the marine site increase with exposure time for this alloy, in marked contrast to the usual pattern of declining corrosion rate with time. It is also curious that the measured loss of strength at the rural PA site is disproportionately large for its corrosion rate (1.4% vs 2.0% at the industrial site).

The bronze alloys were exposed at the same time and place as the zinc during the period 1958-1978, with measurements at 2, 7 and 20 year exposures. Examination of the corrosion rates revealed two separate patterns: a marine trend of high initial corrosion rate with sharp reduction in rate after the first few years, and an industrial-rural trend of constant or increasing corrosion rate over the time period. These trends correspond to different chemical mechanisms at work, with only the industrial-rural corrosion being related to sulfur compounds.

The corrosion rates over distinct time periods are given below. The three sets of rates correspond to the initial two years of exposure, the 5 years covering the period from 2 to 7 years after exposure, and the final 13 years for the period of 7 to 20 years after exposure.

Site	Zinc			1% Bronze			5% Bronze		
	2	5	7	2	5	7	2	5	7
Kure Beach, NC	.77	.81	.30	.51	.40	.18	.92	.49	.30
Point Reyes, CA	.26	.05	.13	.26	.04	.09	.55		.13
Newark, NJ	.68	1.11	.56	.42	.38	.33	.34	.51	.51
State College, PA	.18	.24	.23	.20	.14	.15	.14	.14	.20

Although ratios of the accumulated weight losses do not show a consistent pattern, the discrete time periods do show a sudden agreement after the initial 7 year exposure period. During the last 13 years, the ratio of bronze to zinc corrosion rates (in mdd) falls into the range $0.65 \pm .05$ for both the marine and nonmarine sites for the 1% alloy, with marine values of 1.00 and nonmarine values of $0.90 \pm .03$ for the 5% alloy. These ratios correspond to factors of the coefficients for Cl^- and SO_2 , respectively, in damage functions such as proposed by Benarie (1985). An additional bronze alloy containing 7% Al was examined, and no such relationship was found. Clearly the behavior of a bronze is strongly dependent upon the alloy; it appears that the phosphor bronzes exhibit corrosion behavior quantitatively similar to that of zinc after the first few years of exposure.

6. SUMMARY

A project was undertaken to perform retrospective reconstruction of environmental histories at the sites of previous long term atmospheric metal exposures. The effort required development of appropriate emission information and dispersion modeling capabilities on both the regional and urban spatial scales. The development of useful urban scale emission inventories dating back several decades proved to be a limiting factor. At present, therefore, the retrospective reconstruction of environmental histories is not possible for the large number of sites in the metals corrosion data base. This precludes derivation of damage functions at this time.

Examination of the metal corrosion data base itself has indicated that the reported corrosion values for zinc and bronze, at least, may be associated with regional pollution as well as local SO_2 sources. It also was found that zinc and two tin-phosphor bronzes behave similarly after an initial period of exposure to the atmosphere.

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